CHEMISCHE WERKE HÜLS A.G.

Hüls, Germany. 19 April 1945.

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COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE

CONFIDENTIAL

REPORT ON CHEMISCHE WERKE HÜLS A.G. HÜLS, GERMANY

19 April, 1945

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CIOS Black List Item - 22
Miscellaneous Chemicals

COMBINED INTELLIGENCE OBJECTIVES
SUB-COMMITTEE
G-2 DIVISION, SHAEF (REAR) APO 413

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REPORT ON CHEMISCHE WERKE HÜLS A. G. HÜLS, GERMANY

1. GENERAL.

a. Hüls is one of the important synthetic rubber plants in Germany and has been investigated thoroughly from that standpoint. Our interest was confined to acetylene and styrene, although the following chemical products are made in this plant:-

Acetylene
Ethylene (from Acetylene)
Aldol
Acetaldehyde
Kybol
Styrene
Hexanetriol
Solvents A and AH
Acetophenone
Resin SAX (from styrene, acetophenone, xylene, hydrofluoroboric acid)
Ethylene oxide
Glycol
Glycerine D
Triglycol
Resin AP for surface coating (acetophenone, formaldehyde, methanol)
C acid (crotonic)
Plasticizer 111 (butyl crotonate, hydrogen, sulfide)

2. ACETYLENE MANUFACTURE.

The plant produces 150,000 cu meters acetylene per day by arc cracking.

a. Raw Materials

There have been three sources of raw materials:-

(1) Natural gas from Bentheim used directly

92% CH_4
3% $H_2S + CO_2$
5% N_2

(2) Coke oven gas which was first put through the Linde apparatus.

4e-

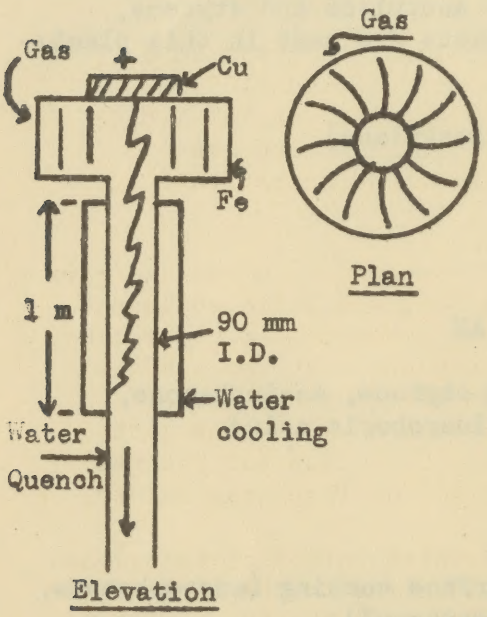
(3) Gas from Hydrierwerke containing 85% hydrocarbons averaging $C_{1.4}$ which was used directly.

b. Power

Power consumption is 8.5 kwh per kg crude acetylene and 9.5 - 10.5 kwh per kg pure acetylene.

AC at 6,000 V 50 cycles is converted in a mercury rectifier to 7,000 V DC at 7,000 kw. Each arc uses 7,000 kw and produces 4,200 cu m/hr product gas. The plant has 17 arc units.

c. Arc Apparatus. (Sketch below)



The gas at 1.5 atmospheres enters the top section at the side and is whirled by the vanes into the arc tube. The arc is not constant in position but rotates around in the tube. Immediately on leaving the arc section, the gases are quenched by water spray to 150°C.

At this point the composition is:-

H_2.....55%
C_2H_2.....13% (1% diacetylene)
C_2H_4.....1%
CH_4 (other H.C.).23%
CO_2, N_2, etc.....8%

d. About 3% carbon is produced based on the original hydrocarbon. The gases pass to four cyclone separators to take out water and carbon, the latter being used in the rubber industry. Further cooling with spray to 70°C takes place and then the gases go through 8 filter towers equipped with cloth bags. The temperature is then reduced to 25°C and the gases washed with tar oil to remove aromatic hydrocarbons such as naphthalene and polymerized hydrocarbons. To regenerate the tar oil it is blown with waste gases (nitrogen, CO and CH_4) from the Linde plant and a side stream distilled with high pressure steam.

5a

Hydrocyanic acid is removed by water scrubbing in tall towers to form a 3% solution which is distilled to recover HCN. Hydrogen sulfide is then removed by passing thru boxes packed with Luxmass (hydrated iron oxide). The gas now containing 20% C_2H_2 passes to a gasometer.

The gas from the gasometer is then compressed to 18 atmospheres in compressors having 4 stages with intercoolers. There are six compressors each handling 13,000 cu m per hr. At this point the partial pressure of the acetylene is 5 atmos. Temperature is reduced to 15°C and acetylene dissolved using 750 cu m of water per 8,000 cu m of gas. Water is also sprayed into the gas lines to avoid explosions. The washed-off gas contains 0.1% C_2H_2.

The pressure of the aqueous solution is dropped in 4 steps to 1.5 and 0.1 atmospheres and to 0.15 and 0.05 atmospheres absolute. Gas from the first step at 50% C_2H_2 goes back to the compressors after mixing with arc gas causing the rise to 20% C_2H_2 in the gas holder mentioned above.

The gas from the 2nd, 3rd and 4th steps are mixed and give 97 - 98% acetylene of which 87% is C_2H_2 and 10% diacetylene and higher. The diacetylene is washed out with tar oil which is blown with Linde gas and the diacetylene sent through the system again. At this point the product gas contains 95% C_2H_2 with 3% hydrocarbon, 1% nitrogen and 1% CO_2. The last traces of diacetylene are removed with 96% H_2SO_4 and the gas neutralized with 10% NaOH and passed to the final gas holder.

The original off gas from the water solution of acetylene step containing 0.1% C_2H_2 passes at 15 atmos to the Linde plant where it is fractionated to 97% pure hydrogen, a mixture of CO and N_2, and a hydrocarbon fraction which after passing through the diacetylene oil washer is joined with the original gas feed to the arc.

3. STYRENE MANUFACTURE.

a. Ethyl Benzene

Ethylation of benzene takes place in 6 enamelled iron towers (with 2 in reserve) 11 m high x 1.4 m diameter operated continuously but not in series. Each tower handles 350 cu m/hr of 95% moist ethylene from a gasometer. They were originally 3/4 filled with Raschig rings but are not now. Ethylene goes in at the bottom through an open pipe and passes

up through the benzene and aluminum chloride. Complete absorption is obtained at 95-105°C with a consumption of 3% $AlCl_3$ on ethyl benzene. No HCl is added since it forms with the moisture of the gas.

The raw ethyl benzene contains:-

35% ethyl benzene
45% benzene
15% polyethylbenzene
5% residue

It passes to a cooler and separator for the $AlCl_3$ complex which is returned to the bottom of the tower. The new $AlCl_3$ is added periodically at the top mixed with benzene. The overflow from the separator is washed with water and then with 1-2% NaOH in a stoneware lined tank. It is settled and dried with solid caustic soda.

Distillation takes place in a series of towers each with a duplicate so that, for instance, No 3 is the second step in the series, No 5 the third, etc. Towers are about 28 meters high and have 45 plates. All except the last are bubble cap plates and last is packed with Raschig rings. Reflux on the ethyl benzene tower is 1:1.

Tower No	Diameter	Temperature	Vacuum	Product
1	0.8 m	--	--	Carbon Bisulfide
3	1.0	80°C	--	Benzene
5	1.6	--	--	Intermediate
7	1.1	136°C	--	Ethyl benzene
9	0.8	130°C	20-25 mm	Polyethyl benzene
11	--	200°C	25 mm	Residue

Polyethylbenzenes are returned to the ethylator.

b. Dehydrogenation of Ethyl Benzene to Styrene.

The catalyst chambers for dehydrogenation are vertical cylinders in brick settings fired with gas on two sides. The 12 chambers are of various types some having 22 to 26 tubes of 20 cm diameter, others 90 tubes of 10 cm diameter and are 2 m diameter x 3 m high. They contain 2 cu m catalyst of 4 - 7 mm particle size made at Ludwigshafen and of the following approximate composition:-

Zn O	85%
Ca O	5%
Al_2O_3	5%
K_2CrO_4	2%
K_2SO_4	2%

7e

Each converter is first swept out with nitrogen, then fed with a 1-1.5 : 1 ratio of steam to ethyl benzene. The feed is vaporized and preheated by heat exchange with flue gases and product gas. Temperature in the converter is 630° and in the product gas 600°C. Each handles 450 kg/hr ethyl benzene with 33% conversion per pass and 90% yield.

After condensation of the crude product 0.001% hydroquinone is added. This is the only addition of inhibitor.

The crude product containing 38% styrene passes into the middle of the first distilling column, a tower 2 m diameter x 25 m high with 45 plates and operated under 20 mm vacuum. Ethyl benzene passes over the top to re-use. The bottoms go into the middle of the second column which is 2 m diameter x 15 m high with 25 plates and operated under 15 mm vacuum. The overhead containing 38% styrene and 62% ethyl benzene is returned to the first column. The crude styrene bottoms testing 102.5% on account of the residues goes into the middle of the first final distillation tower and thence to the second. These towers are 1.1 m diameter x 15 m high, some packed and some plate and run under 15 mm vacuum. 99.5 - 99.8% styrene is taken overhead. There are two sets of two towers for preliminary and the same for final distillation, one presumably for stand-by.

Capacity of the plant is 120 tons/mo per catalytic converter or 1440 tons/mo total.

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